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Intermolecular Hydride-Transfer Reaction. III. Friedel-Crafts Reaction of Aromatics with 1-Phenyl-2-propanol and Related Compounds¹⁾

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The Friedel-Crafts reactions of benzene and of toluene with 1-phenyl-2-propanol and the related compounds were examined. The reaction of toluene with 1-phenyl-2-propanol yielded 1-tolylpropanes as a predominant reduced product, accompanied with 1,1-diarylpropenes as oxidized products. The hydride transfer reaction was found to be a subsequent reaction to follow fast alkylation and relatively slow dealkylation. It is also found that the existence of a protic acid is the necessary condition for the hydride-transfer path. It is concluded that the ionization of the alcohol proceeds more slowly than the dealkylation, while the ionization of the chloride proceeds faster than the dealkylation.

KEY WORDS: Friedel-Crafts alkylation/ 1-Phenylpropanols/ Inter-molecular hydride-transfer/ Oxidation-reduction

INTRODUCTION

It is well known that the Friedel-Crafts reactions are sometimes accompanied with undesired reactions to yield complex product mixtures.²⁾ One of these side-reactions is an intermolecular hydride-transfer reaction. This reaction was well known and many papers have appeared on the formation of reduced products.³⁾ Only a few oxidized products have, however, been confirmed, one of which is 9,10-diethylanthracene obtained in the reaction of benzene with allyl chloride.⁴⁾ We examined the reaction of benzene with 1-phenyl-2-propanol, 1-phenyl-2-chloropropane and the related compounds, and found that the formation of a novel oxidized product, 1,1-diphenylpropene, together with 1-phenylpropane (a reduced product), and 1,1- and 1,2-diphenylpropanes.^{1a)} At almost the same time, the formation of the same oxidized product was reported by Ackermann and Heesing in the reaction of benzene with allyl alcohol,⁵⁾ and also by Matsuda and Shinohara in the reaction of benzene with 2-chloro-1-propanol and its derivatives.⁶⁾

Concerning the mechanism of the formation of this oxidized product, we agreed with these two research groups with respect that the hydride-transfer took place from 1,1-diphenylpropane to 1-methyl-2-phenylethyl cation (a phenonium-type ion).⁷⁾ Although they argued that the phenonium-type ion reacted *concurrently* with benzene and a hydride ion, we have already pointed out the possibility that the ions formed by losing a phenyl group from 1,1- and 1,2-diphenylpropanes abstract a hydride ion from 1,1-diphenylpropane.

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In the course of our studies on the Friedel-Crafts reactions, we found that the reaction of toluene with 1-phenyl-2-propanol yielded 1-tolylpropanes as the predominant reduced products. In this paper, we will report on the Friedel-Crafts reactions of benzene and of toluene with 1-phenyl-2-propanol and the related compounds, and will show that the hydride-transfer reaction is the *subsequent* reaction to follow the fast alkylation and the relatively slow dealkylation.⁸⁾

RESULTS AND DISCUSSION

The reaction of toluene, a large excess, with 1-phenyl-2-propanol in the presence of aluminum chloride was carried out at 40°C for 2 h, and gave benzene (*ca.* 50%), 1-phenylpropane (2%), and a complex mixture of 1,1-diarylpropanes (*ca.* 4%), 1,2-diarylpropanes (*ca.* 35%) and 1,1-diarylpropenes (*ca.* 10%). The results were shown in Scheme 1. Sixty to seventy percent of the diaryl fraction⁹⁾ consisted of ditolyl-substituted materials, that is, 60–70% of phenyl group in the starting material was substituted with a tolyl group. This fact suggests that the tolylpropyl moiety of phenyl-tolylpropanes initially formed was transferred to toluene releasing benzene. The reaction of toluene with 2-chloro-1-phenylpropane gave a similar result.

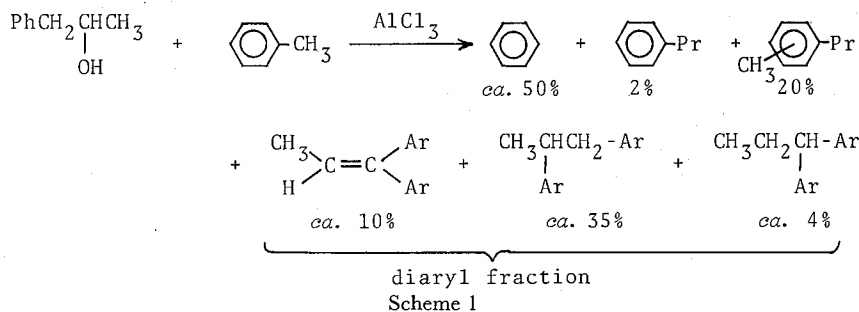
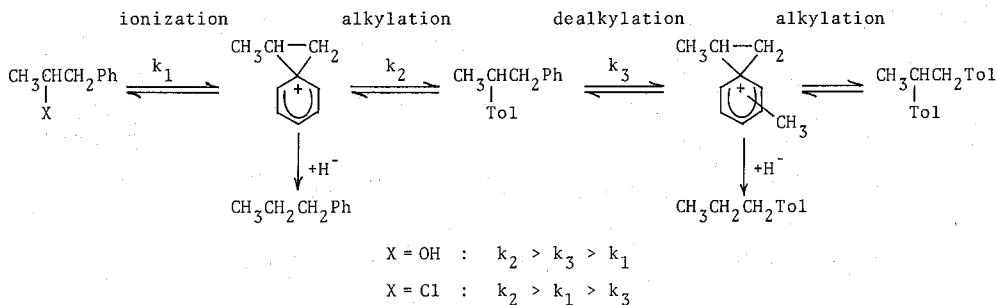


Table I. Reduced products of the reaction of toluene with 1-phenyl-2-propanol and 2-chloro-1-phenylpropane

Alkylating agent	Reaction time (min)	Conversion (%)	Yield (%)		Isomer ratio of Pr-C ₆ H ₄ -Me		
			Pr-C ₆ H ₅	Pr-C ₆ H ₄ -Me	<i>o</i> - (%)	<i>m</i> - (%)	<i>p</i> - (%)
$\text{CH}_3\text{-}\underset{\text{OH}}{\underset{ }{\text{CH}}}\text{-}\underset{\text{Ph}}{\underset{ }{\text{CH}_2}}$	20	22	0.0	0.0	—	—	—
	30	28	0.1	1.6	2.2	44.6	53.2
	45	70	0.5	11	5.3	64.9	29.8
	60	100	1.7	17	6.5	65.1	28.4
	120	100	2.8	23	7.5	65.2	27.3
$\text{CH}_3\text{-}\underset{\text{Cl}}{\underset{ }{\text{CH}}}\text{-}\underset{\text{Ph}}{\underset{ }{\text{CH}_2}}$	2	36	0.0	trace	—	—	—
	5	~100	trace	4.1	0.0	42.4	57.6
	10	100	0.04	8.7	2.4	53.2	44.4
	20	100	0.2	9.8	4.4	64.7	30.9
	30	100	0.7	12	5.0	65.0	30.0
	120	100	1.2	14	6.5	65.0	28.5

In this reaction, the reduced products, 1-phenylpropane and 1-tolylpropanes, appeared slightly after the diaryl compounds. The approximate yields of 1-phenyl- and 1-tolylpropanes and the isomer distributions of the latter compounds are shown in Table I. The amounts of these compounds began to increase after the starting materials had completely disappeared. Isomer distributions of 1-tolylpropanes formed from 1-phenyl-2-propanol were substantially constant after 70% conversion of the starting alcohol, but those from 2-chloro-1-phenylpropane reached to constant values long after the starting chloride disappeared. The GLPC spectrum of the diaryl fraction at 70% conversion of the alcohol (45 min) was already similar to that of the final product (2.5 h), while, in the case of the chloride, the spectrum of the reaction mixture at the completion of conversion (5 min) was still simple and then it became to show a complicated one similar to that of the product from the alcohol. The product of the reaction with the chloride indicating the simple GLPC spectrum was a mixture of 1-phenyl-1-tolylpropanes and 1-phenyl-2-tolylpropanes.

In a reaction process depicted in Scheme 2, the halogen-carbon bond is ionized more readily than the carbon-oxygen bond, and these ionizing processes are assisted by the neighboring phenyl group.¹⁰⁾ Subsequent alkylation proceeds faster than ionization, and *para* position of toluene seems to be favorable to this kinetically-controlled alkylation. Initially formed phenyltolylpropanes are protonated and then release benzene yielding tolylpropyl cations. These cations react with toluene to form 1, 2-ditolylpropanes, or abstract a hydride ion yielding 1-tolylpropanes. The formation of the thermodynamically-controlled products before the disappearance of 1-phenyl-2-propanol indicates that the dealkylation proceeds faster than the ionization of carbon-oxygen bond, while the formation of kinetically-controlled products in an early stage of the reaction with 2-chloro-1-phenylpropane indicates that the ionization of carbon-halogen bond proceeds faster than the dealkylation.



As the 1-methyl-2-phenylethyl cation, a phenonium-type ion, rearranged to the more stable 1-phenylpropyl cation (path b in Scheme 3),¹¹⁾ 1-phenyl-1-tolylpropanes can be formed before the disappearance of 2-chloro-1-phenylpropane.

The reaction of benzene with 1-*p*-tolyl-2-propanol in the presence of aluminum chloride at 40°C for 2 h afforded 1-phenylpropane (19%), 1-tolylpropanes (1%), diphenylpropanes (*ca.* 66%), phenyltolylpropanes (*ca.* 1%), 1,1-diphenylpropene (*ca.* 3%), 1-phenyl-1-tolylpropanes (*ca.* 1%). The product distributions in the course

of reaction are shown in Fig. 1. Initially formed phenyltolylpropanes increased until the conversion of starting material completed, and then decreased to 5% in 20 min. Diphenylpropanes appeared while the starting alcohol still remained, and then increased continuously. 1-Phenylpropane appeared slightly after the appearance of diarylpropanes and gradually increased. These results support the mechanism which implies the reversible arylation of the arylpropyl cations.

Table II. Reduced products of the reaction of benzene with 1-tolyl-2-propanols

1-Tolyl-2-propanol	Yield (%)		Isomer ratio of Pr-C ₆ H ₄ -Me		
	Pr-C ₆ H ₅	Pr-C ₆ H ₄ -Me	<i>o</i> - (%)	<i>m</i> - (%)	<i>p</i> - (%)
<i>o</i> -	19	0.6	14.8	67.2	18.0
<i>m</i> -	22	0.8	20.4	67.6	12.0
<i>p</i> -	19	0.7	13.0	68.4	18.6

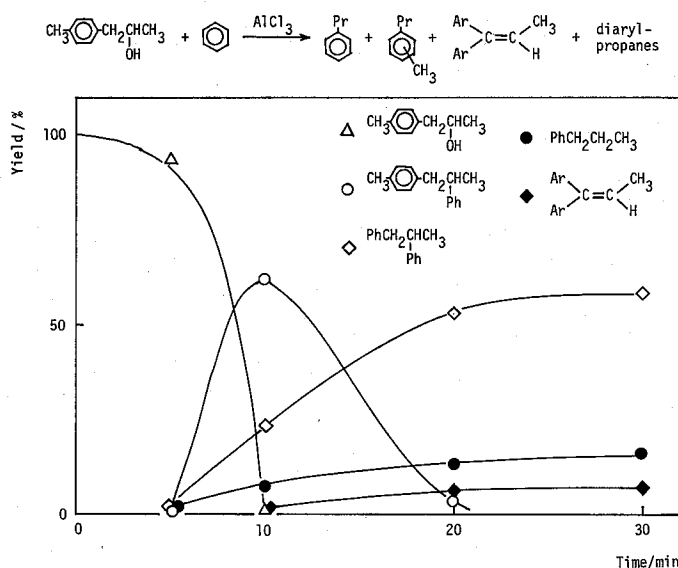


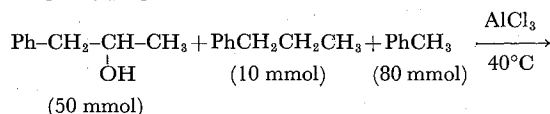
Fig. 1. Products distribution profile of the reaction of benzene with 1-tolyl-2-propanol

The reduced products in the reaction of benzene with 1-(*o*-, *m*-, and *p*-tolyl)-2-propanols are shown in Table II. The ratios of 1-phenylpropane to 1-tolylpropanes are essentially the same, whichever the starting material is. There are no remarkable discrepancies in the isomer distributions of 1-tolylpropanes produced from the three isomeric starting alcohols.

It was proved that the formation of diarylpropanes was a reversible reaction, but it was uncertain whether that of the reduced products was also reversible or not. So the reaction of toluene with 1-phenyl-2-propanol in the presence of 1-phenylpropane was pursued. The results are shown in Table III. 1-Phenylpropane began to

decrease at about 30% conversion of 1-phenyl-2-propanol and then decreased continuously, whereas 1-tolylpropanes appeared at about 14% conversion of the starting alcohol and increased abruptly. This result indicates that 1-phenylpropane released a hydride ion forming phenylpropyl cations, that is, the formation of the reduced products is also reversible reaction.

Table III. Reaction of toluene with 1-phenyl-2-propanol in the presence of 1-phenylpropane



Reaction time (min)	Conversion (%)	Pr-C ₆ H ₅ (mmol)	Pr-C ₆ H ₄ -Me Yield (%) ^{a)}
1	0	10	0
2	8	10	0
5	14	10	trace
10	30	9.2	3.2
15	76	4.5	18
20	100	3.2	24
30	100	2.3	28
60	100	2.4	32

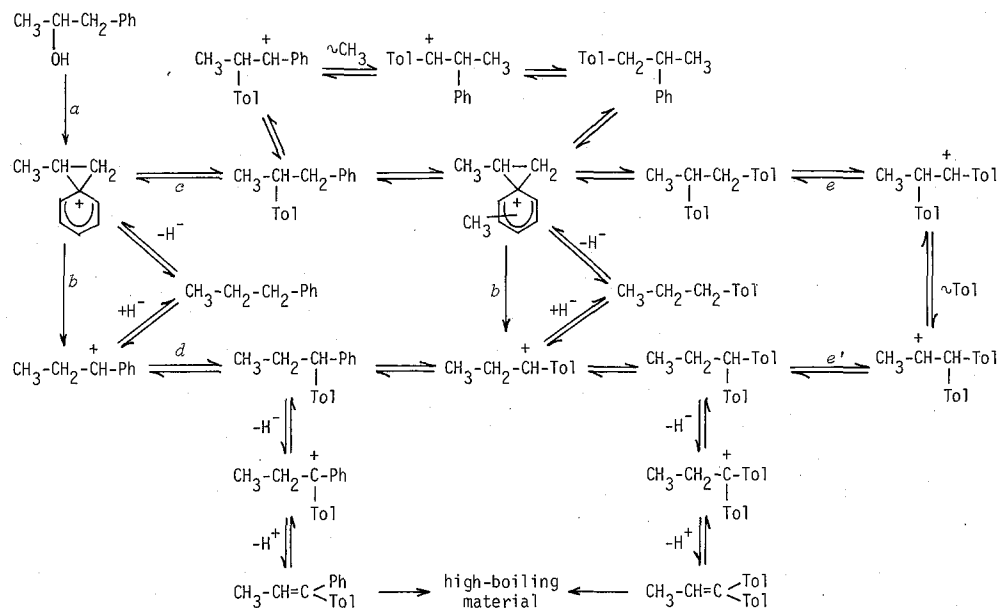
a) Based on 1-phenyl-2-propanol.

It is well known that the Friedel-Crafts reactions were often accompanied with transalkylation, fragmentation, and other side-reactions as well as the hydride-transfer reaction. The present discussion is based on an assumption that no direct transalkylation takes place in the reactions described here. The reaction of toluene with 1-*m*-tolyl-2-propanol in the standard reaction conditions gave only 1-tolylpropanes (22% yield) as the reduced products, and neither 1-phenylpropane nor 1-xylylpropane could be detected in the reaction products. This result clearly indicated that transmethylation, *i. e.*, the direct transalkylation did not take place under the reaction conditions discussed here.

The over-all reaction sequence for the reaction of toluene with 1-phenyl-2-propanol is summarized in Scheme 3. This mechanism can be applied to the reactions of aromatics with allyl alcohol, 2-chloro-1-propanol, 1, 2-dihalopropanes, and many other alkylating agents.^{1a, 5, 6)} The deuterium-scrumbling reaction reported by Ackermann and Heesing can also be explained by this reaction mechanism.⁵⁾ The hydride-transfer reaction is the *subsequent* reaction to follow the fast alkylation and the relatively slow dealkylation. The dealkylation gives arylpropyl cations which abstract a hydride ion from 1,1-diarylpropanes forming arylpropanes, and 1,1-diarylpropanes are transformed to resonance stabilized 1,1-diarylpropyl cations. This cations are transferred to the oxidized products, 1,1-diarylpropene, by losing a proton.

We have reported that neither dealkylation nor hydride-transfer reaction occurs in the reaction of benzene with allylbenzene under the same conditions as described

Hydride-Transfer Reaction Accompanied by Friedel-Crafts Reaction



here.^{1a)} These two contrasted results obtained in the reactions of allylbenzene and of phenylpropanols indicate that a protic acid is essential for the dealkylation and the subsequent hydride-transfer reaction.

In a previous paper, we reported the aluminum chloride-catalyzed reactions of benzene with 1-phenyl-1- and -2-propanols in the presence of oxidizing and of hydride-donor reagents.^{1b)} With the addition of copper(II) chloride as an oxidizing reagent, the yield of 1-phenylpropane was remarkably diminished as expected, but the yield of 1,1-diphenylpropene, an oxidized product, did not increase. The yield of the alkylation products was much higher than that in the case without the additive. These results indicate copper(II) chloride to prevent the oxidation-reduction reactions. Furthermore, in the presence of copper chloride, the reaction with 1-phenyl-1-propanol afforded 1,1-diphenylpropane alone, and 1-phenyl-2-propanol gave a mixture of 1,2- and 1,1-diphenylpropanes but the ratio of the former in the product was higher than that in the case without the copper salt. These results seem to indicate that the rearrangement of the phenonium-type ion to the more stable 1-phenylpropyl cation (path b in Scheme 3) is irreversible, the rearrangement probably takes place *via* the path c.

The addition of *trans*-decalin increased the yield of 1-phenylpropane, and gave a trace of the Friedel-Crafts alkylation product. It is thus indicated that the arylpropyl cations abstract a hydride ion from decalin easier than from 1,1-diphenylpropane and other product, *i.e.*, decalin is very reactive as a hydride donor.

EXPERIMENTAL

^1H -NMR spectra were taken on a JEOL PMX-60 (60 MHz) or a Varian HR-220 (220 MHz) apparatus in CDCl_3 , and chemical shifts were recorded ppm down field from internal TMS. IR spectra were taken on a Hitachi EPI-G2 spectrophotometer. GLPC analyses were carried on a Hitachi 163 apparatus using PEG-20M 5% on Chromosorb W 4 m column.

Materials. Benzene and toluene were washed with conc. H_2SO_4 , and distilled over CaH_2 . Commercial GR grade aluminum chloride was used without further purification. 1-Phenylpropane, 1-phenyl-1-propanol, and 1-phenyl-2-propanol were commercially available, and used without further purification. 2-Chloro-1-phenylpropane was prepared from 1-phenyl-2-propanol and SOCl_2 . Three isomers of 1-tolyl-2-propanol were prepared by the reaction of *o*-, *m*-, and *p*-tolyllithium with propylene oxide, respectively: *o*-, bp 89–93°C/3 mmHg; *m*-, bp 90–92°C/4 mmHg; *p*-, bp 89–90°C/3 mmHg.

The reaction of toluene with 1-phenyl-2-propanol. To a stirred mixture of toluene (60 ml) and AlCl_3 (60 mmol), a solution of 1-phenyl-2-propanol (50 mmol) in toluene (20 ml) was added at once at 40°C. The reaction mixture was stirred at 40°C. The 1.0 ml aliquots of the reaction mixture were taken out at appropriate time intervals, and each aliquot was poured into a mixture of ice-water (1.0 ml), toluene (2.0 ml) and *p*-methoxytoluene (10 mg, as an internal standard). The toluene layers were separated and dried over MgSO_4 and submitted to GLPC analysis. Results are shown in Table I. The stirring was continued for 2 h, and the resulting mixture was poured into water, extracted with diethyl ether, dried over MgSO_4 , and distilled under a reduced pressure yielding the diaryl fraction, bp 134–142°C/5 mmHg. The products distribution of this fraction was determined by integrals of terminal-methyl signals of the ^1H -NMR spectrum: 1,1-diarylpropanes, $\delta=0.85$ (t); 1,2-diarylpropanes, $\delta=1.17$ (d); 1,1-diarylpropenes, $\delta=1.73$ (d). The content of ditolyl-substituted materials was determined by integrals of singlet at $\delta=2.27$ and phenyl protons centered at $\delta=7.0$ in the NMR spectrum.

The reaction of benzene with 1-tolyl-2-propanol. To a stirred mixture of benzene (60 ml) and AlCl_3 (60 mmol) was added at once a solution of 1-*p*-tolyl-2-propanol in 20 ml of benzene at 40°C. The changes of products distribution with the reaction times were examined similar to the case of toluene with 1-phenyl-2-propanol.

The reaction of toluene with 1-phenyl-2-propanol in the presence of 1-phenylpropane. A solution of 1-phenyl-2-propanol (50 mmol) and 1-phenylpropane (10 mmol) in toluene (60 ml) was added to a mixture of AlCl_3 (60 mmol) and toluene (20 ml) at 40°C. The conversion of the alcohol and yields of the reduction products were determined by the similar way to that used in the reaction of toluene with 1-phenyl-2-propanol.

The reaction of toluene with 1-m-tolyl-2-propanol. Into a stirred mixture of AlCl_3 (15 mmol) and toluene (20 ml), a solution of 1-*m*-tolyl-2-propanol (12.5 mmol) in 10 ml of toluene was added at 40°C. The mixture was stirred at 40–55°C for 2 h, and then poured into water. After the usual work-up, the crude product was analyzed by GLPC

using *p*-methoxytoluene as an internal standard.

Identification of the products. Identity of all products was established by IR, ¹H-NMR spectra, and comparison with the reported data, and also done by comparison of their GLPC retention time with those of authentic samples.

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